EXHIBIT 3

BMR—12-02

RN2-11-27.2

The Research Foundation of State University of New York
University at Albany
Office of Technology Development

NEW TECHNOLOGY DISCLOSURE

Please submit completed form to Campus Office of Technology Development

1. CAMPUS SUBMITTING THIS DISCLOSURE
CNSE, University at Albany and SUNY New Paltz

2. TITLE Molecular Organometallic Resists for EUV (MORE):

Tin and Bismuth Compounds

3. KEY WORDS: Organometallic, Molecular Resist, Cluster, EUV, Lithography, Oxalate, Tin, Bismuth

4. TYPE

X Invention   ☐ Software   ☐ Video   ☐ Other

5. PRIMARY CONTACT (*among developers/inventors*)
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6. DATE OF CONCEPTION
June 28, 2011

7. SPONSORSHIP

☐ United States Government   ☐ Private Industry   ☐ SUNY   ☐ RF of SUNY   ☐ Personal

☐ Other _____

Name of Sponsor(s)	Research Foundation or Campus Account Number	Sponsored Assigned Identification Number
Intel, SRC	11 0 00 71	

8. PUBLIC DISCLOSURE

a. Has the description of the technology been published?   ☐ Yes   **X** No   Date: / /

Has the description of the technology been submitted
for publication?   ☐ Yes   **X** No   Date: / /

Title of Publication_____
Title of Journal/Other (*specify*)_____

b. Has the technology been presented at a conference

or professional Meeting?   ☐ Yes   **X** No   Date: /   /

C.   Technology *was* not presented.

9.   BRIEF TECHNICAL CONFIDENTIAL DESCRIPTION (*including its unique features*) *ATTACH ANY MANUSCRIPTS,*

REVIEWS, PAPERS, DIAGRAMS, CHARTS, ETC.

Our invention is to use organo-tin and organo-bismuth compounds or polymers as resists for use in Extreme Ultraviolet Lithography (13.5 nm, EUVL).

We have shown that thin films of organometallic/inorganic compounds with high EUV OD and high mass densities can be used as high resolution, low LER EUV photoresists which we will refer to as MORE (Molecular Organometallic Resists for EUV). This invention focuses on the development of MORE resists containing tin and bismuth metals.

Tin. Three categories of tin compounds have been developed for use as MORE resists: Sn-1, Sn-4 and Sn-12.

Sn-1 compounds contain a single tin atom and are expected to reductively eliminate upon exposure. We have investigated Sn-1 compounds containing a Sn^{IV} center bound to two butyl groups, exploring ligands capable of reductive elimination.

Sn-12 clusters are oxoclusters containing twelve tin atoms found to undergo EUV photochemistry in our preliminary trials, and for which we continue to investigate possible mechanisms. We have investigated Sn-12 clusters through anionic ligand exchange and containing butyl, phenyl and allyl organometallic groups.

Sn-4 clusters are oxoclusters containing four tin atoms that were discovered while exploring new synthetic methods for preparing Sn-12 clusters and are expected to undergo similar photochemistry. We have investigated Sn-4 clusters containing butyl, phenyl and allyl organometallic groups.

Bismuth. Two categories of bismuth compounds have been developed for use as MORE resists: Bi-1 and bismuth clusters.

Bi-1 compounds contain a single bismuth atom and are expected to reductively eliminate upon exposure. We have investigated Bi-1 compounds containing a Bi^{V} center bound to three phenyl groups, exploring ligands capable of reductive elimination.

Bismuth clusters are oxoclusters of bismuth containing 6 or 9 bismuth atoms. To date all of this class of compounds have been found to have poor coating abilities and have not been tested.

Our best organometallic Tin-based resist was our Tin-12 Oxocluster with an oxalate counter-anion (see below). Although current results show poor sensitivity, this organometallic resist film shows good LER and has much promise.

$$[(RSn)_{12}O_{14}(OH)_6][C_2O_4]$$

30 nm h/p
Esize ~ 100mJ
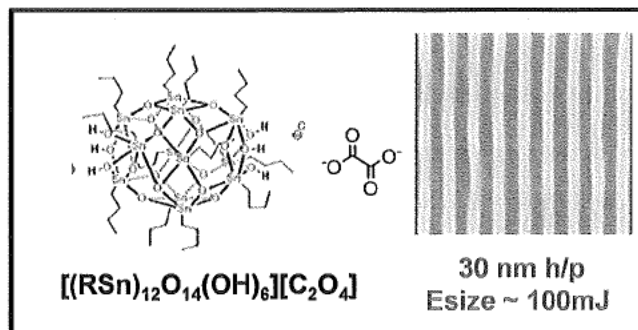
For a detailed description of this invention, please see Appendix A.

10. PROTOTYPES AND/OR SAMPLES

    a. Is a working prototype available for demonstration?   ☐ Yes X No ☐ N/A

    b. Are samples (e.g. compounds) available for testing?   ☐ Yes X No ☐ N/A

11. ADVANTAGES OF THE TECHNOLOGY (*relative to existing technology*)

1. MORE resists should have tight control over particle size, have long shelf-life, lower etch rates and lower particle defects than conventional resist platforms.
2. MORE resists should have extremely high resolution imaging in EUV.

For a detailed description of this invention, please see the Appendix A.

12. POSSIBLE DISADVANTAGES OF THE TECHNOLOGY (*relative to existing technology*)

None.

13. NON-CONFIDENTIAL DESCRIPTION OF THE TECHNOLOGY
    (*indicate applications and advantages -- for marketing purposes*)

This invention concerns the development of a high resolution resist technology for printing 10 nm lines using EUV lithography.

14. LIST COMPANIES THAT YOU BELIEVE WOULD BE INTERESTED IN COMMERCIALIZING THE TECHNOLOGY

Company Name	Contact (if any)	Location/Telephone Number
Intel	Wang, Yueh, Ernisse Putna	

Sematech	Mark Neisser	

Appendix A.

Molecular Organometallic Resists for EUV (MORE):
Tin and Bismuth Complexes

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and Robert Brainard[a]

a. CNSE, University at Albany
b. Department of Chemistry, SUNY New Paltz

1.0 Executive Summary

The purpose of this three-year program is to invent revolutionary new photoresists based on Molecular Organometallic Resists for EUV (MORE) that will be capable of meeting the needs of the 10-nm node. The proposed work will be to screen a broad selection of materials with the capability of stopping EUV photons in 20-nm films (high EUV OD), and to convert them into secondary electrons with short diffusion lengths causing a photochemical change that will result in negative- or positive-tone imaging. We propose that this approach is the best way to meet the LER and sensitivity needs of EUV resists capable of resolution down to 10-nm half-pitch.

Our best organometallic Tin-based resist was our Tin-12 Oxocluster with an oxalate counter-anion (see below). This inorganic resist film shows nice LER if synthetic purity can be controlled. The sensitivity is quite low, but we think that these materials are capable of providing excellent capabilities once a higher speed exposure mechanism can be discovered.

$[(RSn)_{12}O_{14}(OH)_6][C_2O_4]$

30 nm h/p
Esize ~ 100mJ
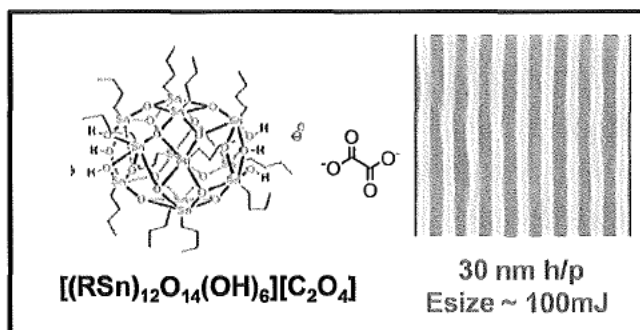
2.0 Results and Discussion

2.1 Tin Compounds

Tin compounds have myriad literature examples, high EUV optical densities (OD) and low redox potentials, making them ideal candidates for MORE. Although the tin literature is vast, few examples exist involving photochemistry--none involving exposure to EUV light. The goal of this work is to investigate tin compounds as candidates for MORE through the exploration and modification of known tin complexes.

To date, 26 tin compounds have been tested and grouped by tin content into three categories: Sn-1 compounds, Sn-4 clusters and Sn-12 clusters. The Sn-1 compounds contain a single tin atom and are expected to reductively eliminate upon exposure. The Sn-12 clusters are oxoclusters containing twelve tin atoms found to undergo EUV photochemistry in our preliminary trials, and for which we continue to investigate possible mechanisms. The Sn-4 clusters are oxoclusters containing four tin atoms that were discovered while exploring new synthetic methods for preparing Sn-12 clusters and are expected to undergo similar photochemistry. The following text will describe the preliminary syntheses and results for each of these three resist types.

2.1.1 Sn-1 Compounds

Initial Designs of Sn-1 Compounds. Due to the known photochemistry of metal oxalates and early successes by our collaborators, early investigations into Sn-1 compounds focused on the development of tin oxalates, but these compounds were found to have poor solubility. Tin dioxalate has been used as a polymerization initiator and cross-linker, but is also extremely insoluble.[1-3] To find a more soluble tin oxalate, we investigated organotin oxalate complexes with soluble, lipophilic organic groups. One patent reported the synthesis of dibutyltin oxalate *via* the hydrolytic exchange reaction between the commercially available dibutyltin oxide and oxalic acid.[4] We repeated this reaction, and found an insoluble solid was produced. To confirm this insolubility, we repeated the synthesis through an alternate tin hydride pathway. Tin hydrides are known to react with carboxylic acids to yield tin carboxylates and elemental hydrogen.[5] Dibutyltin dihydride was synthesized by a previously published route.[6] When the dihydride was combined with oxalic acid, an insoluble white precipitate was formed. Due to the insolubility of products from both reactions, we think dibutyltin oxalate is too insoluble for use (Figure 1A).

Development of Sn-1 Solubility Hypothesis. Through experimentation with alternate Sn-1 compounds, we developed a hypothesis on solubility. Three other Sn-1 compounds were synthesized using formic acid, catechol and *tert*-butyl catechol. Catechol, like oxalate, formed an insoluble precipitate, *tert*-butyl catechol formed a semi-soluble solid, and formic acid formed a soluble, semi-crystalline solid (Figure 1B). We think these tin compounds form 6-coordinate complexes which can dramatically affect solubility. The dibutyltin oxalate is constrained to a 4-coordinate complex, allowing intermolecular coordination, ultimately resulting in the formation of an insoluble network structure. The dibutyltin diformate however, can orient itself such that the carbonyl oxygens are coordinating with the tin, preventing crosslinking and resulting in a significantly more soluble product (Figure 1C).
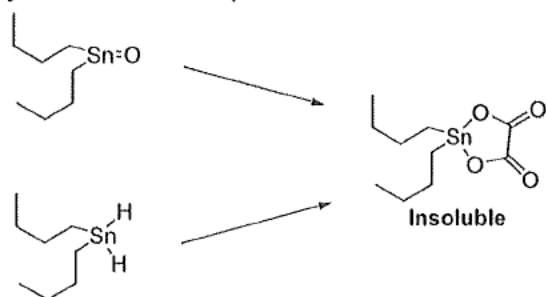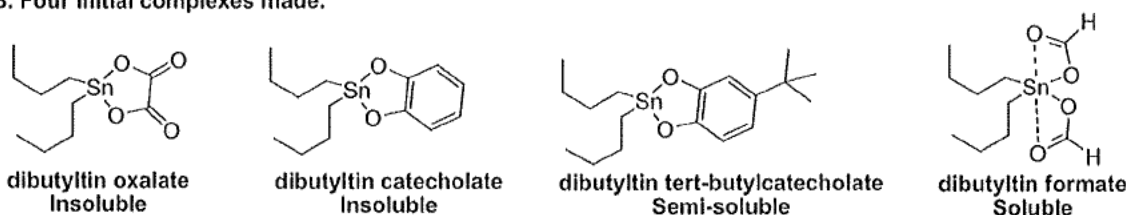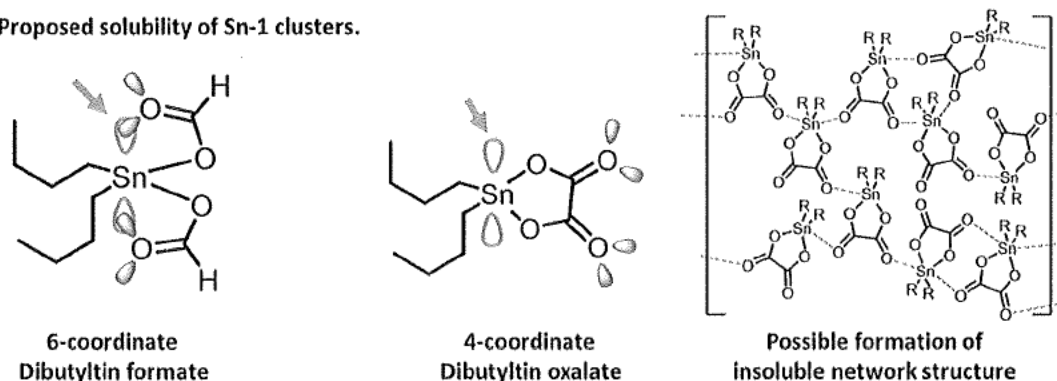
A. Synthesis of Sn-1 complexes

B. Four initial complexes made.

| dibutyltin oxalate Insoluble | dibutyltin catecholate Insoluble | dibutyltin tert-butylcatecholate Semi-soluble | dibutyltin formate Soluble |

C. Proposed solubility of Sn-1 clusters.

6-coordinate
Dibutyltin formate

4-coordinate
Dibutyltin oxalate

Possible formation of
insoluble network structure

Figure 1. Synthesis of four Sn-1 clusters. A. Two synthetic pathways to create the dibutyltin oxalate both resulted in an insoluble precipitate. **B.** Four Sn-1 clusters were synthesized, of which, only one had good solubility properties, most likely due to the formation of a 6-coordinate tin. **C.** The lone-pair carbonyl electrons can reach around, forming a soluble monomeric structure for the dibutyltin diformate. The lone-pair electrons on the oxalate, however, are constrained from intramolecular rearrangement to fill the empty tin binding sites. This forces intermolecular coordination to occur, resulting in an insoluble, network structure.

Sn-1 Solubility Hypothesis and Preliminary Lithographic Evaluations. In order to test the 6-coordinate solubility hypothesis, and to evaluate EUV photosensitivity, twelve Sn-1 compounds were synthesized and evaluated (Figure 2). Although all twelve compounds were evaluated for solubility and film-forming capability—not all have been exposed due to time constraints during our most recent trip to PSI. All tested compounds showed some photosensitivity, however due to mask failure, poor mechanical film properties and not-yet-understood effects of the film, none properly resolved the interference patterns. The trend in solubility, however, correlates with our hypothesis; compounds that can form 6-coordinate systems have excellent solubility properties.
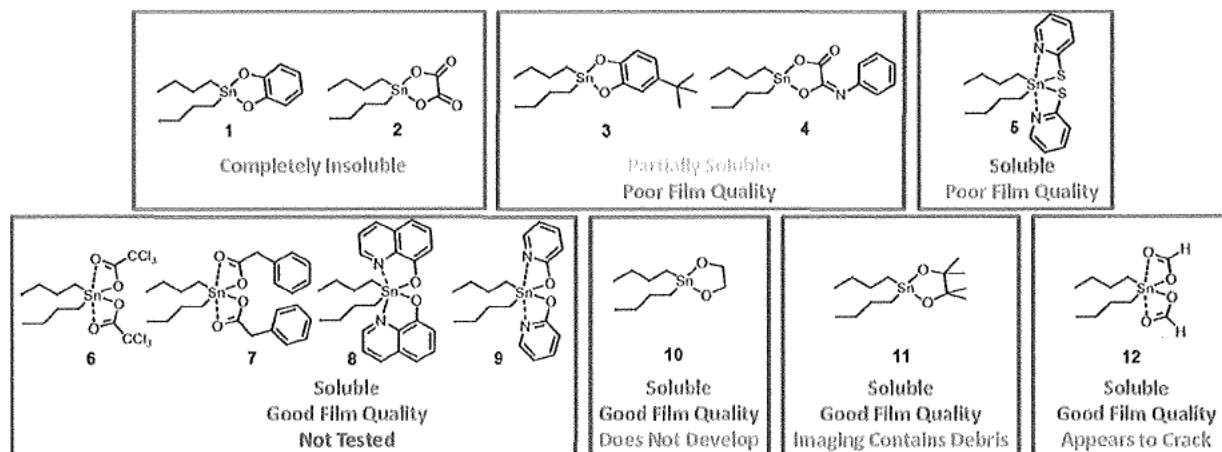
Figure 2. Twelve Sn-1 compounds made and tested with some general results.

Interesting Results from PSI. Of the twelve compounds listed above, dibutyltin diformate (**12**) and dibutyltin pinacolate (**11**) gave the more interesting results (Figure 3A). The diformate produced a low-magnification pattern in the SEM, however upon inspection of the patterned area, no lines were produced. Furthermore, this film appears to be riddled with cracks and tears which are most likely a result of poor mechanical properties. The pinacolate also formed a low-magnification pattern, and on closer inspection appears to resolve lines, however the formation of a second nanoscale-structure appears to have formed intermixed with the lines (Figure 3B). As of yet, the cause of this secondary structure is unknown, but may be due to resist impurities or partial crystallization of the film. Although no imaging was obtained from the Sn-1 clusters run at PSI, each resist tested did appear to have photosensitivity. With more time and development, this class of compounds may prove to be successful.
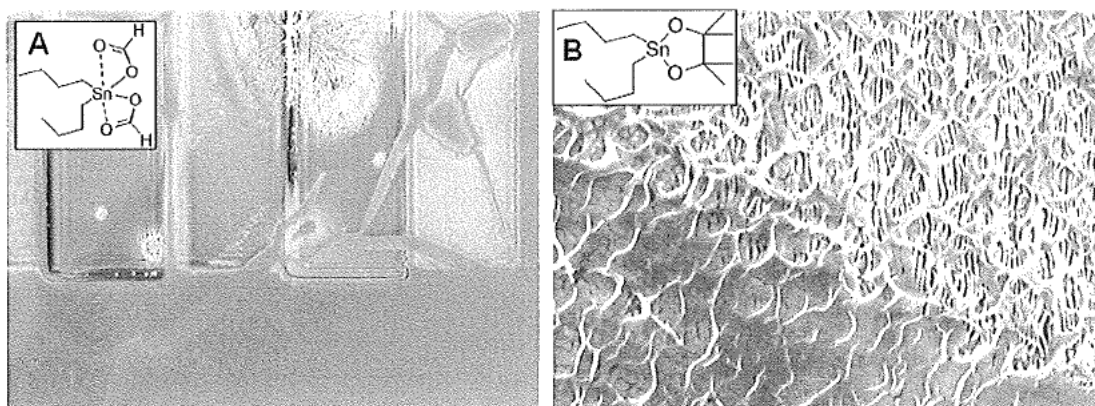
Figure 3. SEM results of two Sn-1 clusters. **A.** The diformate was found to produce a low-magnification pattern, although on careful inspection, no lines are present. Furthermore, cracking of the film is evident. **B.** The pinacolate does appear to have generated lines, however there also seems to be a secondary structure incorporated in with the lines. As of yet, the cause of this debris is unknown.

Probable Mechanism for Sn-1 Cluster Photolysis. A possible mechanism the Sn-1 compounds undergo during exposure is likely the reductive elimination shown is Figure 4. This would produce the

tin(II) complex and the dimeric ligand product. In the case of most carboxylates, the ligand product would be the high energy peroxide. By tuning the oxidation potentials of the groups bound to the tin, we predict the photosensitivity of these compounds can be tuned. Currently, the syntheses of alternate Sn-1 compounds are being performed to evaluate the probability of this mechanism, and to improve image quality.

Figure 4. Possible reductive elimination reaction due to exposure of Sn-1 clusters.

2.1.2 Sn-4 Clusters

During the development of novel Sn-12 clusters, smaller compounds were formed which we think are oxoclusters containing only four tin atoms (Sn-4). The hydrolysis of butyltin trichloride has been studied for the synthesis of Sn-12 clusters and side products ranging from single mononuclear compounds to insoluble network structures are known.[7] Our synthetic strategy for making novel Sn-12 clusters involved the hydrolysis of one of several alkyltin trichlorides followed by determination of reaction products using gel permeation chromatography (GPC). Upon hydrolysis of phenyltin trichloride two soluble clusters were found, the Sn-12 cluster $[(PhSn)_{12}O_{14}(OH)_6][Cl]_2$ and the Sn-4 cluster $(PhSn)_4O_6$. Furthermore, we found that by changing the reaction conditions, the formation of one cluster could be favored over another.

Synthesis and Preliminary Evaluation. A series of three Sn-4 clusters were synthesized and lithographically evaluated at PSI. Using similar hydrolysis conditions and varying the starting organotin trichloride, phenyl (Sn-4A), butyl(Sn-4B) and allyl(Sn-4C) clusters were made containing four tin atoms. Figure 5B shows the preliminary lithographic results for these compounds. Both Sn-4A and Sn-4B showed preliminary imaging, while Sn-4C showed a latent image without dissolution contrast. With further work, we think we can improve the image capabilities of these resists as well as gain insight into the photoreaction of the Sn-12 compounds.
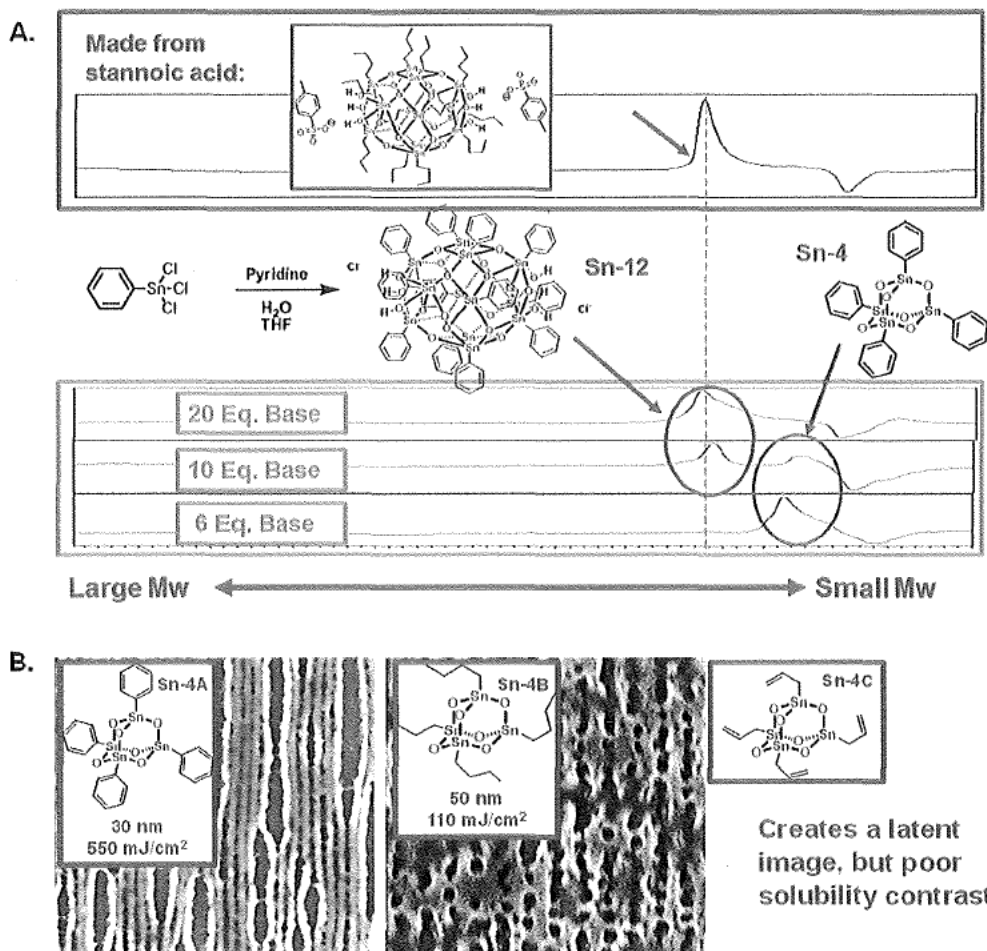
Figure 5. The synthesis and imaging results of three Sn-4 clusters. **A.** GPC results showcasing how the base concentration can control the size of the cluster created. **B.** Three Sn-4 clusters were made and tested containing phenyl (Sn-4A), butyl(Sn-4B) and allyl(Sn-4C) organic groups. Sn-4A and Sn-4B both show imaging, but more work is needed. Sn-4C appears to be sensitive, but solubility contrast was not achieved.

2.1.3 Sn-12 Clusters

Compounds described as $[(RSn)_{12}O_{14}(OH)_6][X]_2$ are very well known with 37 references.[7-43] These compounds have been used as tin oxide precursors, esterification catalysts and as organometallic hybrid materials. Preliminary testing of these clusters show negative-tone sensitivity to EUV exposure, but with relatively low sensitivity. To improve the capabilities of this system, we continue to investigate how varying different aspects of structure affects the EUV sensitivity and image quality.

Structure and Predictions on Photoreactivity. The Sn-12 cluster has a "football-shaped" cage structure,[43] containing 12 tin atoms. Each tin has one bond to carbon and four or five bonds to oxygen. At each side of the structure are three hydroxyl groups, and each cluster has a +2 net charge which is accompanied by two anionic ligands. We predict that there are three likely mechanisms that could cause a solubility change during exposure: anionic ligand decomposition, homolysis of the Sn-C bonds, and metathesis of the Sn-O framework (Figure 6). To evaluate each of these three reaction pathways,

we continue to investigate the effect of changing different components of these clusters, and observing the influence that change has on the lithographic sensitivity and overall performance.
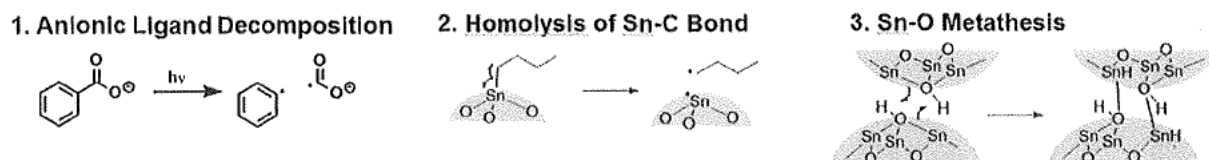
1. Anionic Ligand Decomposition   **2. Homolysis of Sn-C Bond**   **3. Sn-O Metathesis**

Figure 6. Three Possible Mechanisms for Photo-Reactivity. The Sn-12 cluster has three possible components that could cause a change in solubility upon exposure: anionic ligand decomposition, homolysis of Sn-C bonds, and metathesis of the Sn-O framework.

Anionic-Ligand Decomposition:

One possible reaction that could occur during exposure is the decomposition of the anionic ligand. Each Sn-12 cluster has a charge of +2, and therefore also has two mono-anionic ligands. Since organic carboxylate salts are known to undergo a "Norrish type I" decarboxylation reactions with UV light,[44-49] we reason that similar photodecomposition reactions could occur using EUV and result in imaging.

Synthesis and Litho Results. A series of Sn-12 clusters were prepared with sulfonate and carboxylate anionic ligands.[36] $[(BuSn)_{12}O_{14}(OH)_6][TsO]_2$ (**18**) was made by hydrolysis of butylstannoic acid. This compound was tested lithographically and was also a synthetic intermediate for preparing the carboxylate complexes. The carboxylate complexes were prepared by first converting the tosylate complex (**18**) to the hydroxide complex, $[(BuSn)_{12}O_{14}(OH)_6][OH]_2$, then reacting it with stoichiometric quantities of carboxylic acids to produce the carboxylate clusters. These clusters were spin-coated onto silicon wafers and their Egel values were determined using the direct contrast tool (DCT) on the BMET (Figure 7). The photosensitivity of these cluster films correlates with the size of their anions. This may indicate that the exposure mechanism involves the interaction between tin oxo-clusters and that the anions are unreactive spacers between these clusters.
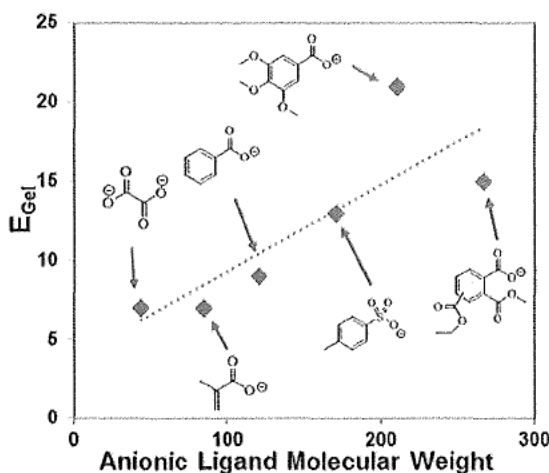

Figure 7. Anionic ligand size *vs.* photospeed of $[(RSn)_{12}O_{14}(OH)_6][X]_2$ complexes. The photospeed seems to correlate more with ligand size, favoring smaller ligands, than expected decarboxylation reactivity. More samples are needed to confirm this relation.

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Sn-12 Oxalate Results. To date, the Sn-12 oxalate cluster shows the best imaging (Figure 8). Our preliminary results showed very good image quality for all features on the mask (from 100 nm to 30 nm h/p). When retested at PSI with a higher resolution mask, the image quality of the first trip was not reproduced. We have studied this reproducibility problem and think that one source of starting material is impure. Nonetheless, despite the poor LER in the most recent experiments, it is clear that this system is capable of giving reasonably good resolution (~18 nm resolution and 16 nm modulation). Further work is needed to determine the full capabilities of this resist.
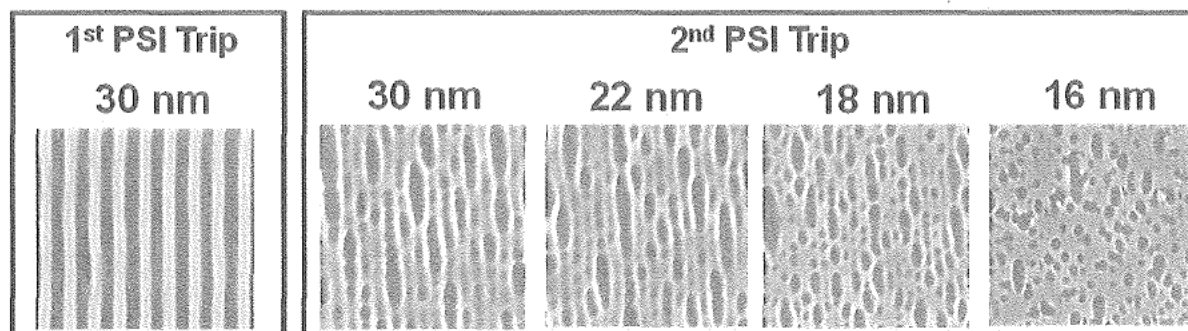
Figure 8. PSI interference imaging of BuSn-12 Oxalate $[(RSn)_{12}O_{14}(OH)_6][ox]_2$. The 1st PSI Trip was performed on a mask containing h/p resolutions from 100 nm to 30 nm and imaged at an effective dose of 110 mJ/cm^2. The 2nd trip to PSI was run on a mask containing h/p resolutions from 30 nm to 16 nm and imaged at an effective dose of 140 mJ/cm^2.

Homolysis of the Tin-Carbon Bonds. A second possible reaction that could occur during exposure is homolytic cleavage of the alkyl-tin bond. Tin-carbon bonds are relatively weak (only ~50 kcal/mol), and tin forms extremely stable radicals,[50] therefore it is conceivable that EUV exposure could cause homolysis. If homolysis occurs, we predict that stabilizing or destabilizing the organic radical should result in a change in the photosensitivity of the cluster. Figure 9 shows a series of organic groups with their associated C-H bond dissociation energy.[51] The bond dissociation energy of the C-H bond should correlate with the relative radical stability of the organic group. The goal of this study is to synthesize a series of Sn-12 clusters containing alkyl groups with different radical stabilities, and to then test these clusters for sensitivity and imaging.

Figure 9. The bond dissociation energies for five organic groups. By incorporating these groups into the Sn-12 clusters, a broad distribution of Sn-C bond energies should be achieved.

Synthetic Studies. Few literature examples involve the synthesis of Sn-12 clusters with different alkyl groups, and so an exploration of the Sn-12 synthesis was necessary. Sn-12 clusters have been synthesized by either the dehydration of butylstannoic acid or the controlled hydration of butyltin

trichloride. Since butylstannoic acids are generally made from the butyltin trichloride, our goals involved purchasing or making alkyltin trichlorides followed by hydrolyzing these compounds. The most common method for making butyltin trichloride is by the radical-mediated Kocheshkov redistribution reaction which involves the superheating of the tetrabutyltin and tetrachlorotin to ~200 °C.[52, 53] This same reaction with the allyl organic group, however, proceeds quickly at 20 °C.[54] The distilled allyltin trichloride product has been scaled up to beyond 20 g of ultimate product; phenyltin trichloride and butyltin trichloride were purchased and used directly.

Synthesis of Novel Sn-12 Clusters. Initially, we modified two literature procedures for preparing the Sn-12 clusters with variation in alkyl groups. Our first approach was to hydrolyze phenyltin trichloride to get phenylstannoic acid and to then dehydrate to the Sn-12 cluster. Unfortunately, this procedure only yielded an insoluble white precipitate. From our prior work with these clusters, we knew that this insoluble precipitate could not be our target compound. Our next approach involved the slow hydrolysis of phenyltin trichloride with sodium hydroxide, maintaining a pH of 4.[7, 41-43] With this method, again only an insoluble white precipitate was produced. We then modified this synthetic route to involve a less nucleophilic, amine base. Using an organic amine in water and THF, we found the phenyltin-12 cluster (PhSn-12) could be made in excellent yield, along with the analogous Sn-4 cluster (PhSn-4) as indicated by GPC results. Furthermore, by changing the relative base concentration in the reaction, the product formation could be controlled to form one cluster over another (Figure 5).

Evaluation of Sn-C Bond Homolysis Study. Under similar hydrolysis conditions, three Sn-12 clusters containing phenyl (Sn-12A), butyl (Sn-12B) and allyl (Sn-12C) organic groups were synthesized and tested at the PSI interferometer (Figure 10). Sn-12A appears to have an impurity which is phase separating and creating pockets in the film matrix. Sn-12B and Sn12C both are capable of resolving 30 nm features, however due to mask failure and lack of time more work on these resists is needed.
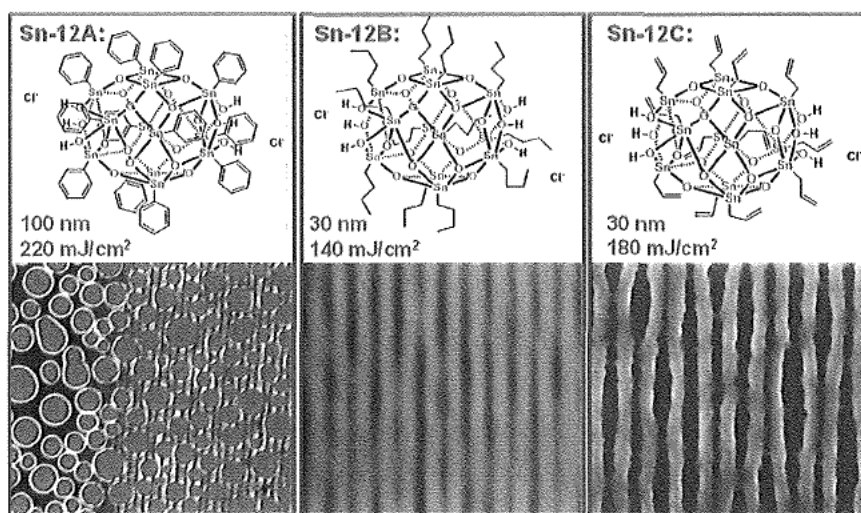

Figure 10. Three Sn-12 clusters were made and tested containing phenyl (Sn-12A), butyl(Sn-12B) and allyl(Sn-12C) organic groups. Sn-12A appears to have purity issues, and phase separation is occurring in the film. Sn-12B and Sn-12C were both capable of resolving 30 nm features but further work is required.

Metathesis of the Tin-Oxygen Framework: A third possible reaction that could occur during exposure is the *intermolecular metathesis* of the tin-oxygen frameworks of two adjacent clusters in which Sn-O bonds rearrange creating bonds between clusters, similar to the reactions that are proposed to occur in HSQ resists.[55-59] At the core of the Sn-12 cluster lies the "football-shaped" cage of tin-oxygen bonds.[43] This core structure is similar to the hydrogen silsesquioxane (HSQ) structure, a known high-resolution resist. Upon exposure, HSQ undergoes a change in solubility by an exchange reaction between a silicon-hydrogen bond in one cluster and a silicon-oxygen bond in another, resulting in crosslinking. Since tin and silicon are both group IV elements, it is likely that a similar metathesis may occur. A tin-oxygen bond of one cluster could exchange with a butyl-tin bond of another cluster, resulting in cross-linking of the clusters (Figure 11).

Investigations of Sn-O Exchange Reactions. Investigation of the occurrence of a metathesis may be challenging. Since the formation of Sn-12 clusters is only known with a tin and oxygen framework, structural modification would be very difficult. Sn^{119} NMR is a very powerful method for the structural determination of tin compounds, and may be a helpful method to investigate the structure of the photoproducts and thus the overall photoreaction. Also, we intend to use GPC to show that dimers are formed.
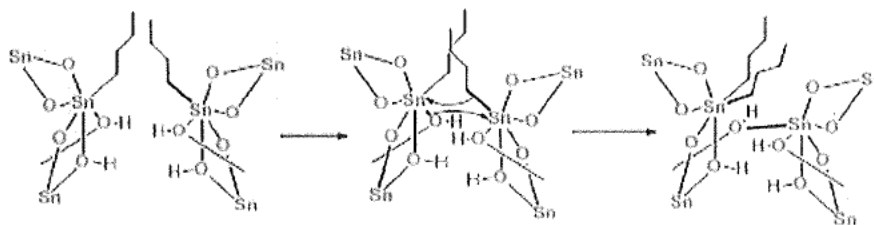
Figure 11. Possible HSQ-like mechanism for cross-linking of Sn-12 clusters. Like HSQ, exposure may cause the metathesis of the tin-carbon bond of one cluster with the tin-oxygen bond of another.

2.2 Bismuth Compounds

Known as the largest, non-radioactive element, bismuth has many properties that make it an excellent candidate for MORE. Bismuth has a high EUV optical density, a high mass density and a very low toxicity. Bismuth compounds have been used in cosmetics, pigments and pharmaceuticals.[60,61] Furthermore, the synthesis of organometallic and inorganic bismuth compounds is well-documented in the literature.

Overall, we have struggled with solubility in our work with bismuth complexes, although we have found some soluble complexes. We have investigated the synthesis of many bismuth clusters, but have found nearly all are far too insoluble to spincoat. Of the soluble clusters, many are highly fluorinated and produce poor quality films. The most successful bismuth compounds to date have been mononuclear organobismuthates which we will refer to as Bi-1 compounds. We have also been exploring the chemistry of soluble clusters containing 6 or 9 bismuth atoms which we will refer to as Bi-6 and Bi-9 clusters, respectively. The following text will describe the preliminary syntheses and results for Bi-1 compounds and prospective plans for the Bi-6 and Bi-9 clusters.

2.2.1 Bi-1 Compounds:

Our Bi-1 compound design consists of a Bi^{5+} central atom capable of reductive elimination. The most common and stable oxidation state for bismuth is +3, however the highly oxidized +5 also exists and is known to be somewhat stable.[62] In order to attain a solubility switch in the Bi-1 clusters, we believe that we can incite a reductive elimination of the highly oxidized Bi^{5+} to a Bi^{3+} accompanied by oxidation of two ligands.

Design and Synthesis. The most common pathway to make +5 bismuth compounds is to oxidize the triphenylbismuth using a chlorinating agent, followed by nucleophilic displacement of the chloride groups.[62] Triphenylbismuth dichloride (Bi-1A) was made from the reaction of triphenylbismuth and sulfuryl chloride (Figure 12). This synthon was then reacted with a series of different nucleophiles in the presence of an amine base. We predict the photoreactivtiy of these compounds involves the reductive elimination of the ligands, and so we expect the resist sensitivity to correlate with ligand structure. To test this, ligands were selected with different functional groups covering a large range of reduction potentials.

Bi-1 Stability. A series of different Bi-1 compounds were made, and the stability of these compounds agrees with a reductive elimination mechanism. When reacted with tert-butyl catechol (Bi-1B) and mercaptopyridine (Bi-1C), the resulting products were both found to be unstable. In both cases triphenylbismuth was recovered, and in the case of Bi-1C, the disulfide was made. These reaction products support the suggested reductive elimination mechanism. Bi-1A was also reacted with hydroxypyridine (Bi-1D), creating a stable compound at room temperature. Upon heating the reaction mixture under vacuum (~80 °C), Bi-1D decomposed yielding triphenylbismuth. When benzoic acid was reacted with Bi-1A, a thermally stable adduct was formed (Bi-1E). Since catechols and thiols are much easier to oxidize than phenols and carboxylates, we would expect these compounds to be much less stable under a reductive elimination mechanism, therefore supporting our predictions.
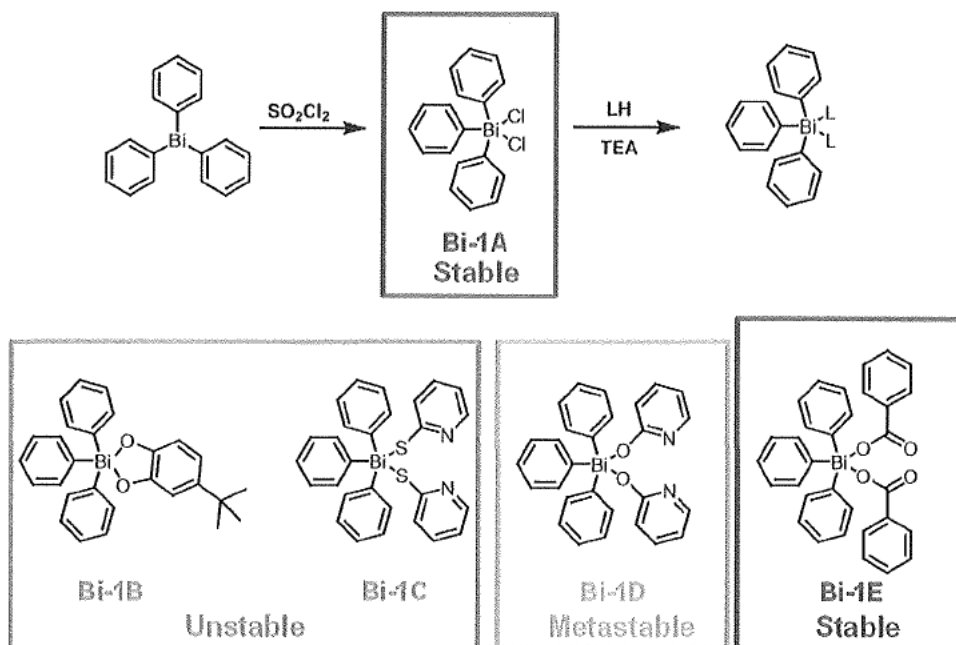
Figure 12. Synthesis and stability of some Bi-1 clusters. A series of Bi-1 clusters were synthesized and the thermal stability was observed. The tert-butylcatechol (Bi-1B) and mercaptopyridine (Bi-1C) adducts were found to be unstable at room temperature. The hydroxypyridine (Bi-1D) adduct was found to be stable at room temperature but unstable when heated. The benzoic acid adduct (Bi-1E) was found to be thermally stable even when heated.

Lithographic Evaluation. Bi-1A and Bi-1E were tested for imaging at the PSI interferometer (Figure 13). Although these results are preliminary, both resists imaged and the dose of Bi-1A (140 mJ/cm^2) is significantly higher than Bi-1E (30 mJ/cm^2). The poor image quality may be explained by the degradation of the mask used during imaging and/or poor mechanical properties of the film. Current work is being done to further test the effect on sensitivity of different carboxylates and alcohols. Plans are also being made to modify the starting triphenylbismuth to improve film mechanical properties.
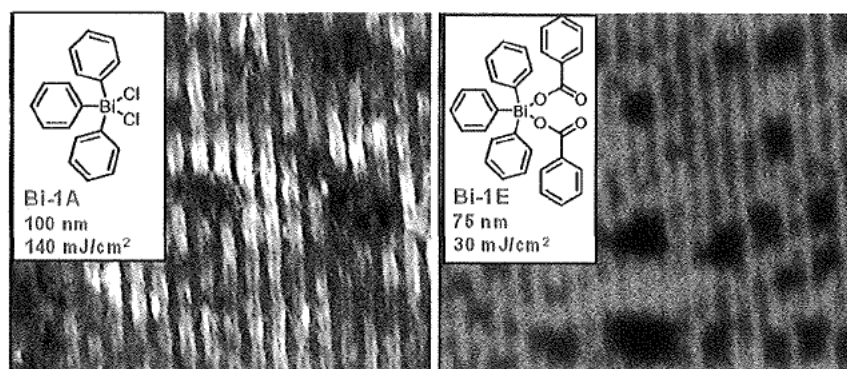
Figure 13. Exposure results of two Bi-1 clusters. Preliminary results indicate that both clusters are imagable, however suffer from poor mechanical properties. Work is being done to modify these clusters to improve mechanical properties and to explore other reductive groups.

2.2.2 Bi-6 and Bi-9 Clusters

Poor Solubility of Most Bismuth Clusters. We have reproduced many bismuth clusters of the type $[Bi_6O_8H_n][X_m]$ reported in the literature, however we have found these clusters face significant solubility issues. All efforts taken to alter these clusters in order to imbue solubility have been unsuccessful thus far, and alternative clusters are being examined.

Soluble, Fluorinated Bi-6 Clusters. Whitmire *et al.* reported the synthesis of a Bi_6O_8 core cluster surrounded by three $(Bi(OC_6F_5)_4)$ and one (C_6F_5) groups (Figure 14A) through the hydrolysis of the phenoxide.[63, 64] These fluorinated aromatic groups lend a tremendous amount of solubility to the cluster enabling it to be dissolved in a number of different solvents. The cluster is made from the slow hydrolysis of the $Bi_2(OC_6F_5)_6$ dimer followed by crystallization. The literature procedure has been replicated and the cluster has been made and found to be very soluble. When attempting to spincoat, however, the highly fluorinated cluster beads off of the wafer. Current work is being done to replace the fluorophenol (OC_6F_5) with non-fluorinated ligands $(OC(CH_3)_3)$ and also to make underlayers that can be used to promote adhesion and to eventually coat these fluorinated clusters.
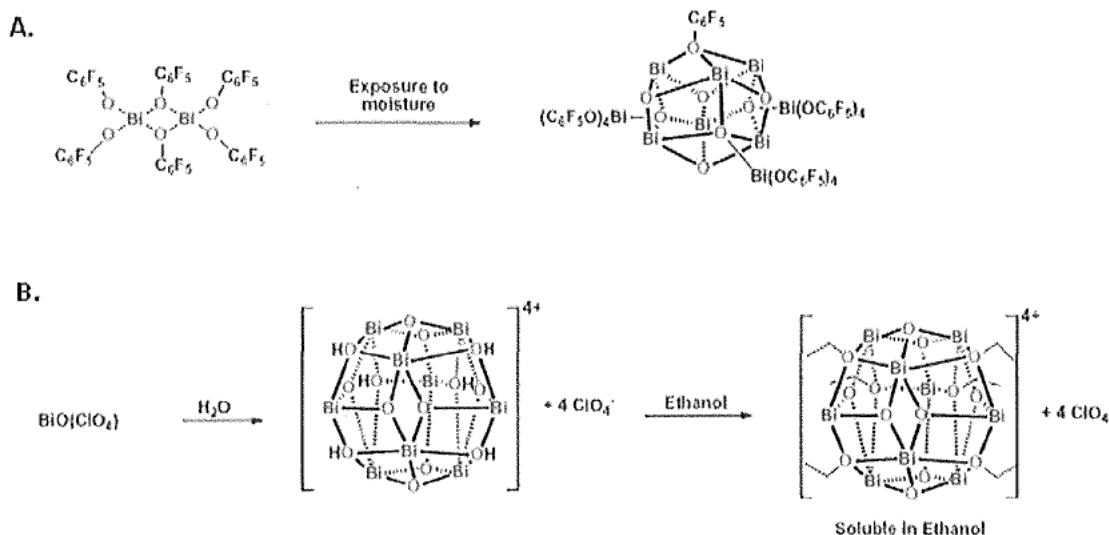
Figure 14. **Current progress toward the synthesis of bismuth oxoclusters.** **A.** By exposing the $Bi_2(OC_6F_5)_6$ dimer to moisture, the soluble Bi-6 cluster can be made. Current work involves modifying the cluster or testing alternate substrates in order to get good coating quality. **B.** By hydrolyzing the $BiO(ClO_4)$ followed by heating in ethanol, a soluble Bi-9 cluster can be made. Current work involves improving the synthesis of the starting $BiO(ClO_4)$.

Synthetic Strategies for Preparing Bi-9 Clusters. An alternative to the Bi-6 cluster is the Bi-9 cluster. Reported by Thurston *et al.*, the Bi-9 cluster can be made by hydrolysis of $BiO(ClO_4)$ (Figure 14B).[65] This cluster itself does not appear to be soluble, however, upon heating in ethanol the hydroxide groups are converted to ethoxide groups making the cluster significantly more soluble in organic solvents. Replication of this work has been attempted, however, with unsuccessful results,

most likely due to impure $BiO(ClO_4)$. Currently, the synthesis of a high purity starting material is under investigation.

2.4 Summary of Results.

2.4.1 Table of Results. Over the course of this work, 32 inorganic and organometallic compounds were made and tested. These compounds have been grouped as three types of tin clusters: Sn1, Sn4 and Sn12 and Bismuthates. The full results of all compounds including coating quality, casting/develop solubility and EUV sensitivity has been disclosed (Table 1).

We have made and tested 32 compounds from six material classes for MORE and the results have been disclosed. In analysis of these results, the following conclusions can be drawn:

- **Bismuth and Tin Compounds can be Made to Reductively Eliminate.** We have developed both Tin and Bismuth compounds that we believe reductively eliminate upon exposure. We continue to optimize these compounds to improve sensitivity and image quality.
- **Bismuth Clusters Have Poor Solubility.** We have reproduced many of the bismuth clusters in the literature, and we have found that most are insoluble. The clusters that are soluble contain fluorine and have poor wetting results. We are currently investigating remaking these clusters with less fluorine and developing fluorinated underlayers to get better coatings.
- **Tin Clusters Show Promising Results.** Tin clusters show the greatest promise, with sub-20 nm imaging. We have identified three possible mechanisms that could occur during exposure: anionic ligand decomposition, homolysis of the tin-carbon bond and metathesis of tin-oxygen bonds. We continue to work towards understanding the mechanism of exposure, as we think this will enable us to improve the sensitivity of these clusters.

Table 1. 32 MORE compounds were made and tested. The results of this testing has been grouped into six categories: Tin Clusters, Bismuthates, Zincates, Metal Acetoacetonates, Metal Halides/Ferricyanides, and Initial Cluster Work.
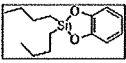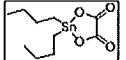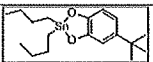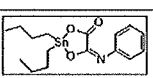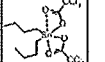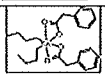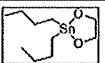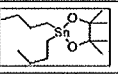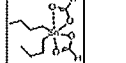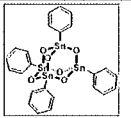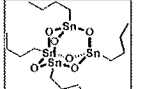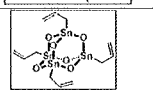
Structure	Name	Compound #	Coating Solvent	Coating Quality	Soft bake	Developing Solvent	Emax (Mj/cm2)	Esize (Mj/cm2)	Resolution (nm)
					Sn-1				
	Sn1 Catecholate	1	Insoluble						
	Sn1 Oxalate	2	Insoluble						
	Sn1 tBuCatecholate	3		Poor Film Quality					
	Sn1 Ox/Aniline Ad.	4		Poor Film Quality					
	Sn1 Thio Pyr	5		Beads up on wafer					
	Sn1 Trichloroacetate	6	Ethyl Lactate	Good		66% IPA/H2O		Did not SEM	
	Sn1 Phenylacetate	7	Anisole	Good				Did not Test	
	Sn1 HydroxyPyr	8	Did not test						
	Sn1 Hydroxy Quinoline	9	Did not test						
	Sn1 Ethylene Glycolate	10	Toluene	Good		Did not Develop			
	Sn1 Pinacolate	11	Toluene	Slightly crystalline		Debris over lines			
	Sn1 Formate	12	Acetonitrile	Film appears to crack		IPA/H2O			
					Sn-4				
	Sn-4A	13	Ethyl Lactate	Poor		50% IPA/H2O		550	30
	Sn-4B	14	Ethyl Lactate	Good		50% IPA/H2O		110	50
	Sn-4C	15	Ethyl Lactate	Good		Overdeveloped			

Table 1. (Cont.)
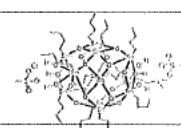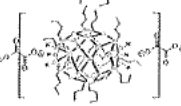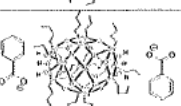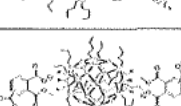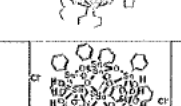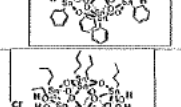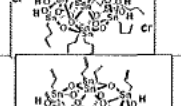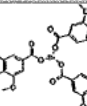
					Sn-12				
	BuSn12 Mesylate	16	Ethyl Lactate		90C/90s		20		
	BuSn12 Oxalate	17	Ethyl Lactate		90C/90s	66% IPA/H2O		140	18
	BuSn12 Tosylate	18	Ethyl Lactate		90C/90s	50% IPA/H2O		180	30
	BuSn12 Benzoate	19	Ethyl Lactate		90C/90s	50% IPA/H2O		180	30
	BuSn12 (OMe)₃Benzoate	20	Ethyl Lactate		90C/90s	50% IPA/H2O		65	50
	BuSn12 (F)₃Benzoate	21	Ethyl Lactate	Did not wet					
	BuSn12 (COOEt)₂Benz	22	Ethyl Lactate		90C/90s	33% IPA/H2O	15		
	BuSn12 Methacrylate	23	Ethyl Lactate		90C/90s	33% IPA/H2O	7		
	PhSn12 Cl (Sn-12B)	24	Ethyl Lactate	Porous	90C/90s	66% IPA/H2O			
	BuSn12 Cl (Sn-12A)	25	Ethyl Lactate		90C/90s	40% IPA/H2O		140	30
	AllylSn12 Cl (Sn-12C)	26	Ethyl Lactate		90C/90s	Tol/THF		180	30

Table 1. (Cont.)

	Bismuthates									
	BiPh₃	27		Did not wet						
	Bi(Benzoate)₃	28						No Sensitivity		
	Bi((Ome)₃Benzoate)₃	29						No Sensitivity		
	Bi((F)₃Benzoate)₃	30						No Sensitivity		
	Ph₃BiCl₂	31							140	100
	Ph₃Bi(Benzoate)₂	32							30	75

5.0 Notes and References

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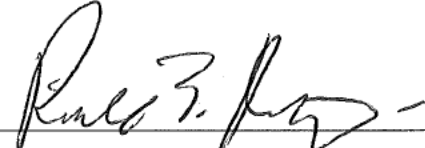Developer's Signature: _____ Date: Feb. 8, 2013

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